

SOLVENTS FOR USE IN THE TREATMENT OF  
LIGNIN-CONTAINING MATERIALS

Field of Invention

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The present invention relates to solvents for use in the treatment of lignin-containing materials, including lignocellulosic materials. Such materials include plant matter and plant matter derivatives. The present invention further relates to methods for extracting useful products from lignin-containing materials, including lignin and optionally other products, and the products obtained by such methods. The present invention additionally relates to new chemical species found to be suitable for use in these processes.

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Background of Invention

Plant products, which are ligno- and lignocellulosic materials, are used by man in the production of a number of different valuable commodities.

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However, the lignocellulosic residues that are produced in large volumes from agricultural cropping of sugar, wheat, rice and corn, for example, are largely considered of little value and, if not collected, are often plowed-in, burnt or otherwise discarded. Some efforts have been made to extract useful materials from such waste lignocellulosic material (biomass). Examples of these processes utilize pretreatment with heat and chemicals followed by enzymatic digestion, or the application of concentrated mineral acids, to extract fermentable sugars and lignin. The derived sugars are intended to provide a feedstock for conversion into a renewable source of greenhouse gas neutral liquid fuels such as ethanol, or other valuable industrial and fine chemicals. Processes contemplated to achieve this have a number of similarities to wood pulping processes, as they may involve

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fractionation and separation of the lignin content from the cellulose, although in the case of the biomass the digestion conditions are more extreme so as to also cause the ultimate breakdown of the cellulose content into smaller chemical products.

There is room for improvement on the known processes for the treatment of lignin-containing material, including the wood pulping methods (the kraft pulping method being most common) and the lignocellulosic biomass treatments.

Novel pulping processes should:

- Manage suitably prepared hardwood, softwood and herbaceous raw materials
- Not degrade cellulose and hemicelluloses
- Preferably require lower temperatures, pressures and pulping times than are usual in conventional pulping
- Utilize known and tested engineering methods and equipment already perfected for conventional pulping, wherever possible
- Have an optimal size smaller than that of a typical pulp mill.

In addition, the resulting pulp should:

- Be directly substitutable by current end-users for conventional pulps with equivalent properties
- Be readily bleachable
- Offer high yield
- Allow valuable by-products to be recovered.

Finally, the process should:

- Have efficient and simple chemical recycling systems
- Close the chemical cycle of the process, with little or no make-up chemical consumption
- Have low specific energy consumption
- Avoid malodorous emissions by being totally sulphur free

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- Permit complete recovery of process water with minimal discharge
- For occupational health and safety, product residue, environmental, and other regulatory and public policy requirements, employ known chemicals that have negligible or low human and environmental toxicity, be non-flammable and non-explosive
- Facilitate economic, environmental and other efficiencies in existing conventional pulping mills, if possible

Various "organosolv" processes have been contemplated as alternatives for the kraft process for the treatment of lignin-containing materials. Few, if any, of these have satisfied enough of the criteria outlined above to be commercially feasible.

The proposed processes for extracting lignin from waste lignocellulosic biomass have also suffered from disadvantages that have prevented any significant commercial adoption of the processes to date.

In the late 1950s McKee (CA 631,051) developed an "organosolv" alternative to kraft pulping which involved pulping under elevated temperature and pressure with a hydrotropic mixture of water and the crystalline salt sodium xylenesulphonate.

While this process appeared to offer some advantages over conventional pulping methods, it still suffered from a number of drawbacks. Under this process, a maximum of 40% of the salt is used in the solvent mixture, and with this hydrotropic system, the maximum temperature that can be attained under atmospheric pressure conditions is not much higher than the boiling point of water. As a consequence of this, to obtain sufficiently extreme conditions to break down the woody material into lignin and other

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byproducts including furfural and acetic acid, it is necessary to conduct the process at elevated pressure. The equipment required to achieve this introduces higher costs and design complications into the process, and makes it difficult to conduct the process continuously.

Consequently, there is room for improvement on the various processes known in the art for the treatment of lignin-containing materials.

#### Brief Summary

The present invention relates to the application of ionic liquids (preferably salts of acids with aryl functionality) as solvents or additives for treating (for example, dissolving, digesting, extracting and/or isolating materials from) natural sources or materials such as lignin-containing materials, including biomass.

Thus, according to a first aspect of the present invention, there is provided a method for the treatment of a lignin-containing material comprising the step of contacting the lignin-containing material with an ionic liquid.

Preferably, the method further comprises the step of extracting lignin from the lignin-containing material into the ionic liquid, and recovering the lignin from the ionic liquid. The material remaining after the lignin has been extracted is either cellulosic fibre that can be further processed into pulp for conversion to paper, or fully degraded to fermentable sugar monomers, or may be referred to as a waste material. According to one embodiment, the cellulosic fibre or waste material is separated from the ionic liquid following extraction of the lignin into the ionic liquid.

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According to a second aspect of the present invention, there is provided the use of an ionic liquid in the treatment of a lignin-containing material.

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According to a third aspect of the present invention, there is provided a product produced by the process described above.

10 Certain ionic liquids contemplated for use in the process of the present invention are novel per se, and therefore according to a fourth aspect of the present invention there is provided an ionic liquid comprising:

- 15 - an substituted or unsubstituted aryl organic acid anion; and
- an ionic liquid-forming inorganic cation or an organic cation.

20 Thus, the present invention also provides the use of the novel ionic liquids in the treatment of natural materials, such as plant materials and plant-derived materials.

#### Brief Description of the Figures

25 Figure 1 is a schematic illustration of a process according to one embodiment of the invention.

#### Detailed Description

##### 30 *Ionic Liquid*

Ionic liquids are organic salts with low melting points (up to 100°C), many of which are consequently liquid at room temperature. Specific features that make ionic  
35 liquids suitable for use in the present invention are their lack of vapor pressure, their ability to dissolve a wide range of organic compounds and the versatility of their chemical and physical properties. In addition,

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ionic liquids are non-flammable, which makes them suitable for use in the industrial applications contemplated by the present application.

5 It has been found that, in addition to these beneficial properties, when contacted with lignin-containing materials such as lignocellulosic materials, including plant matter and plant matter derivatives, the ionic liquids are capable of penetrating these materials, and  
10 removing the lignin therefrom. In addition, with the appropriate choice of treatment conditions (for example, time of contact and temperature), ionic liquids penetrate the structure of the lignin-containing material to break the material down to extract further organic species  
15 making up the lignin-containing material. Any cellulosic component remaining in the lignocellulosic material is preserved. Once separated from the ionic liquid liquor, the cellulosic component may then be optionally broken down into smaller organic compounds such as hexose and  
20 pentose sugars, which can be converted into fuel sources such as ethanol.

Although not wishing to be bound by theory, it is also believed that the ionic liquids contemplated for use in  
25 these applications have surfactant behaviour and/or catalytic ability that make them particularly useful in various embodiments.

Further, ionic liquids remain liquid at high temperatures  
30 without evaporating, when used alone or in high concentrations with a cosolvent. Thus, the ionic liquids can be used in the treatment of lignin-containing materials at high temperature, without the necessary application of pressure. Additional advantages of certain  
35 preferred ionic liquids are their ease of handling and low toxicity.

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The ionic liquid may be a single species, or may be a mixture of different ionic liquid species. The ionic liquid may be used alone, or in combination of a cosolvent. Suitable cosolvents include water and organic solvents such as alcohols, ethers, acids and so forth. Water is particularly suitable.

According to one embodiment, the ionic liquid comprises:

- an substituted or unsubstituted aryl organic acid anion; and
- an ionic liquid-forming inorganic cation or an organic cation.

#### *Anion*

Regarding the anion component, the term aryl denotes single, polynuclear, conjugated and/or fused residues of aromatic hydrocarbon or aromatic heterocyclic ring system. Examples of aryl include phenyl, biphenyl, terphenyl, quaterphenyl, phenoxyphenyl, naphthyl, tetrahydronaphthyl, anthracenyl, dihydroanthracenyl, benzanthracenyl, dibenzanthracenyl, phenanthrenyl, fluorenyl, pyrenyl, indenyl, azulenyl, chrysenyl, pyridyl, 4-phenylpyridyl, 3-phenylpyridyl, thienyl, furyl, pyrrol, pyrrolyl, furanyl, imadazolyl, pyrrolydiny, pyridinyl, piperidinyl, indolyl, pyridazinyl, pyrazolyl, pyrazinyl, thiazolyl, pyrimidinyl, quinolinyl, isoquinolinyl, benzofuranyl, benzothienyl, purinyl, quinazolinyl, phenazinyl, acridinyl, benzoxazolyl, benzothiazolyl and the like. If the aryl in the case of the anion is an aromatic heterocyclic ring system, this suitably contains 1 to 4 heteratoms independently selected from N, O and S and up to 9 carbon atoms in the ring. The aromatic functionality of the aryl organic acid anion may include any hetero-atoms, branched and/or ring fragments with the substituent promoting the solvent properties and/or physical properties of the corresponding ionic liquid.

According to one embodiment, the aryl is a hydrocarbon (ie non-heterocyclic) aryl group, typically phenyl or naphthyl.

- 5 The aryl may be unsubstituted or substituted by one or more substituents. Suitably substituents may be selected from one or a combination of alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, 10 haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitrile, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, imino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, 15 alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio, organic acid or 20 ester such as sulfonate, and the like.

When a substituted aryl is used (preferably phenyl, naphthyl or pyridyl), there are suitably between 1 and 4 substituents, and these are preferably independently 25 selected from the group consisting of alkyl, hydroxy, amino and halo. More preferably the substituents are alkyl. According to one particular embodiment, the substituents are methyl.

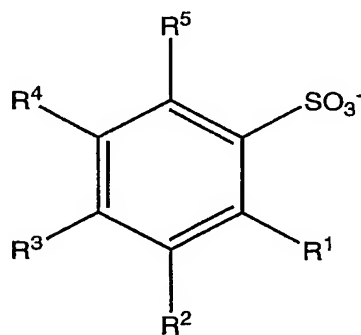
- 30 The term "alkyl" denotes straight chain, branched or mono- or poly- cyclic alkyl, preferably C1-30 alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, hexyl, octyl, dodecyl, 1-methylundecyl and the 35 like. The term halo encompasses chloro, iodo, fluoro and bromo.



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The term "organic acid" in the context of the anion component of the ionic liquid refers the organic acids of sulfur, carbon and phosphorous, and therefore the anion species of these acids (i.e. in which the proton of the acid is removed) encompasses the sulfonates, sulfates, carboxylates, phosphinates, phosphates and so forth. The sulfonates (the anion of the organic acid sulfonic acid) is the subject of a number of embodiments of the present invention. It is noted that the anion may contain more than one organic acid group - such as the aryl disulfonate anions.

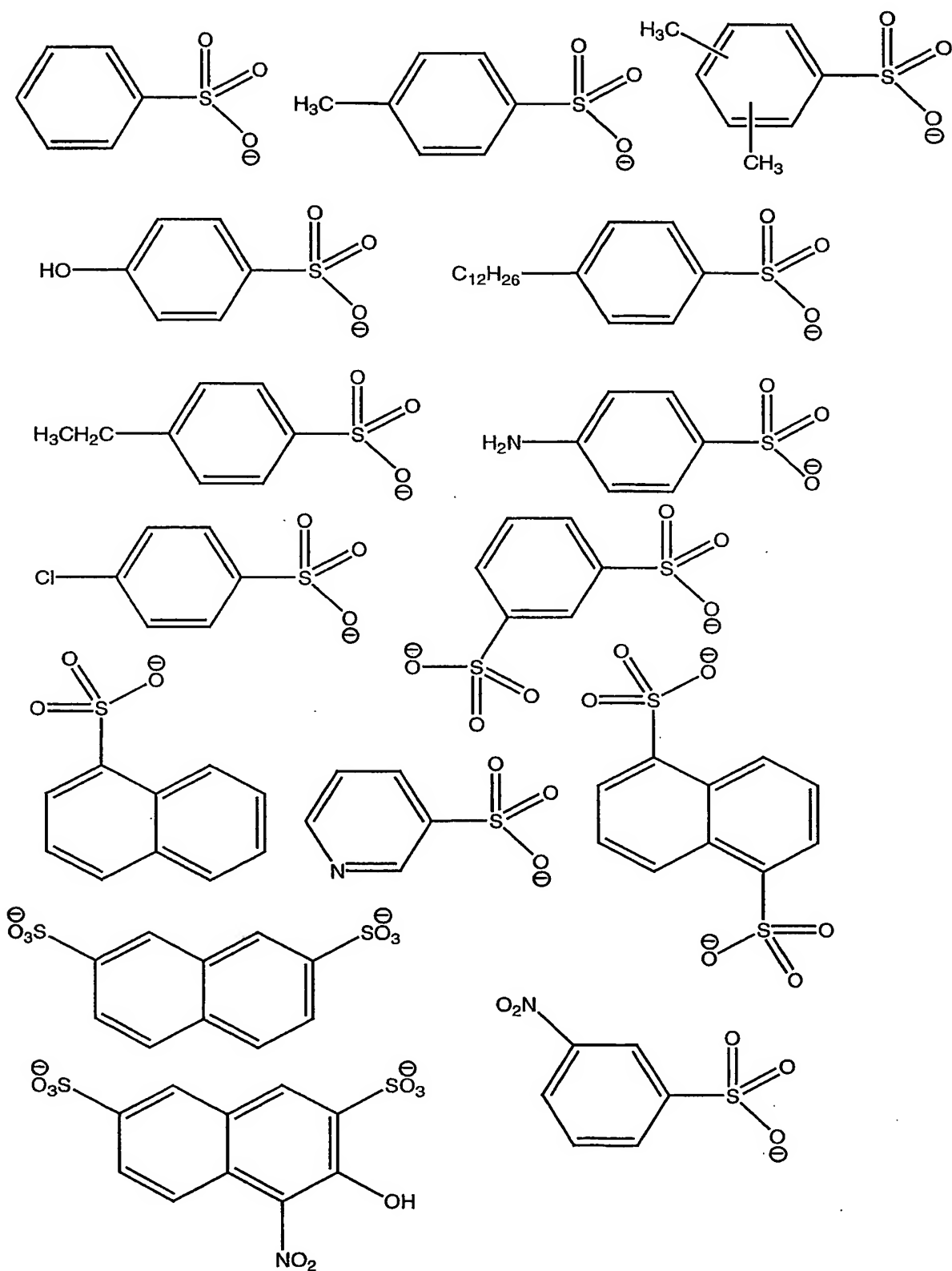
The ionic liquid of one embodiment is thus a salt of arylsulfonic acids. The anions of Formula 1 are examples of this class.



Formula 1

In this structure R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> are each independently selected from the group consisting of hydrogen, alkyl (including but not limited to methyl, ethyl, dodecyl), alicyclyl, aryl (including but not limited to benzyl and naphthyl), aralkyl, alkylaryl, heteroaryl, halogeno, haloaryl and sulfonate. In the case of sulfonate, the dianion may be partially or fully neutralised.

Other examples of anions that may be used are represented below.



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The sulfonates are a particularly useful class of the substituted or unsubstituted aryl organic acid anions. The results set out in the Examples below show that ionic liquids containing anions based on aryl sulfonate group (substituted or unsubstituted) are particularly effective in extracting lignin from the lignin-containing materials.

#### *Cation*

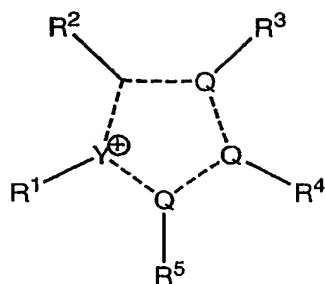
The cation component is either an ionic liquid-forming inorganic cation or an organic cation.

Regarding inorganic cations, it will be understood that simple alkali metals or alkaline earth metal cations that form crystalline salts with the anion component are not within the scope of the present invention, and therefore Na salts are excluded. Suitable inorganic cations include the rare earth metals.

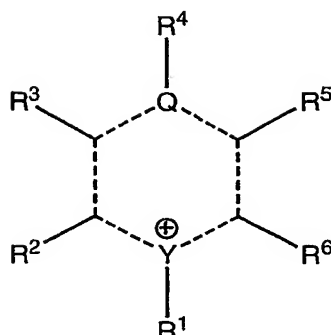
Amongst the organic cations, the present invention encompasses substituted or unsubstituted imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium equivalents of the above-mentioned groups, ammonium, phosphonium and sulfonium cations. In the case of substituted cations, the substituents are preferably selected from one or more of the optional substituents referred to above in the context of the anions, but they are preferably selected from hydrogen, aliphatic (i.e. optionally substituted alkyl, alkenyl, alkynyl), alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, haloaryl.

Some representative examples of the cations encompassed are the cations of Formulae 2 (2a, 2b and 2c) and 3:

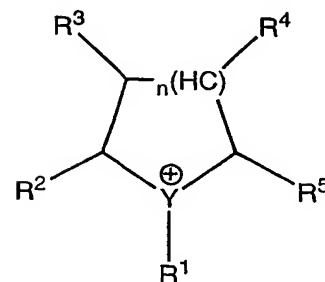
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Formula 2a



Formula 2b



Formula 2c

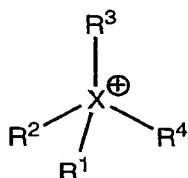
in which:

the dotted lines represent single or double bonds;

Q represents N, CH, O or S, and wherein when X represents  
 5 O or S, the group R is absent and the adjoining bonds are  
 single bonds;

Y represents N or P; and

n is 1 or 2



Formula 3

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wherein:

X represents N, P or S;

R<sup>1</sup> to R<sup>4</sup>, are each independently selected from aliphatic  
 (i.e. optionally substituted alkyl, alkenyl, alkynyl),  
 15 alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl and  
 haloaryl.

Choline and derivatives thereof are other examples of  
 suitable cations.

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Further components which may be included in mixture with  
 ionic liquid contacted with lignin-containing material

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The salts which are the subject of this invention, are generally liquids at some temperature below 250°C either in their pure state or when mixed with one or more other salts. The salts that may be mixed with the ionic liquid  
5 may be a second ionic liquid as described above, or any other known ionic liquid.

The ionic liquids may be used as solvents or additives. When used as a solvent, the solvent may also include a  
10 further component which is a molecular solvent such as water, ethanol, toluene and other solvents well known in the field of chemistry. In some embodiments of the invention, the ionic liquid may constitute between 50 and 100% of the solvent composition, for instance between 70%  
15 and 100% of the solvent composition.

When used as a solvent, the solvent composition may be used in any suitable solvating amount with respect to the lignin-containing material. It may for instance be used  
20 in an amount of between 2 and 50 times the amount of lignin-containing material, based on weight.

Commonly used acids and bases may also be added to this solvent composition for simple pH management of optimal  
25 conditions or other advantageous effect. Such acids or bases may be present at weight percentages from 0.01% - 90%. The pH may be controlled within the range 3.0 to 14.0, suitably 5.0 to 12.0, as required by the process. The more vigorous the conditions, in terms of pH, time and  
30 temperature, the greater the expected penetration of the lignin-containing material for the extraction of lignin and other extractable chemicals.

Any other components may be used in the solvent  
35 composition, including Na and/or Li salts, transition metal or other oxidation catalysts, air or molecular oxygen. Such components (including sodium xylene

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sulfonate) may be used for catalytic effect or otherwise. Such additives may be present at weight percentages from 0.01% - 90%, suitably 0.01 - 10% by weight.

- 5 In an alternative application, the ionic liquids that are the subject of this invention may be used as additives, and therefore they may be added to the composition of conventional kraft alkali liquors to facilitate and accelerate removal of lignin. The new ionic liquids may  
10 be used in the treatment of any natural products to extract extractable chemicals therefrom.

*Natural sources and lignin containing materials*

- 15 The present invention is broadly applicable to the treatment of natural sources, including plant and plant-derived materials. This therefore encompasses lignin-containing materials. The term lignin-containing material encompasses, without limitation, plant derived biomass,  
20 corn stover, sugar cane bagasse and cane residues, rice and wheat straw, agricultural grasses, woodchips, bamboo, and all other materials proximately or ultimately derived from plants.
- 25 Lignin is a complex polymeric material (mostly comprised of phenolic groups, anisole, primary, secondary alcoholic groups and aldehydes) located in the woody cell wall that confer strength and rigidity to the woody cell. In the preparation of paper, the lignin is removed to leave the  
30 cellulosic material for formation into paper.

*Processing steps*

- The ionic liquid is used in the treatment of materials. Treatment encompasses dissolving, digesting, extracting  
35 and/or isolation of components therefrom.

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One suitable treatment comprises contacting a lignin-containing material with the ionic liquid to extract lignin and optionally other chemicals into the liquid phase, and thereafter separating the liquid phase from  
5 remaining solids. In the case where the lignin-containing material is a lignocellulosic material, the remaining solids comprise cellulosic fibre.

The contacting stage is suitably conducted at an elevated  
10 temperature, and preferably at atmospheric pressure. Preferably the this stage is conducted at a temperature between 50 and 200°C, more preferably between 100 - 180°C, most preferably between 120 - 160°C. Preferably the time of contact is between 1 and 8 hours.

15 The lignin-containing material is contacted with the ionic liquid in a vessel, and the contents heated to the desired temperature by any suitable means. One suitable heater is a boiler, which may be powered by any fuel, such as the  
20 lignin recovered during downstream processing of the ionic liquid.

After separation of the liquid phase from the remaining solids, the process suitably comprises the step of  
25 precipitating lignin from the liquid phase. This may be achieved by any of a number of ways, for example precipitation may be induced by adding water and/or varying temperature or pH. Alternatively, the liquid phase may be contacted with an immiscible organic solvent  
30 into which the lignin products report, or with a polyethylene glycol (PEG) solution to form an aqueous biphasic system within which the lignin products will preferably move to the organic PEG phase. Thereafter the precipitated lignin is recovered from the liquid phase,  
35 for example by filtration, or from the immiscible organic solvent by distillation, or from the PEG phase of the biphasic system by pH adjustment followed by filtration.

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The recovered lignin may be used as a fuel or feedstock for this or any other process.

Once the extractable chemicals such as lignin have been  
5 extracted into the ionic liquid, and thereafter removed,  
the ionic liquid can be recovered by any suitable means  
from the process liquor (i.e. re-concentrated and  
separated from contaminants), or alternatively reused  
directly. Recovery can be achieved by a number of  
10 methods, including, without limitation, salting out with  
an appropriate inorganic salt (e.g. Potassium phosphate  
salt), reverse osmosis, or solidification by temperature  
reduction. The last of these examples is of particular  
interest for ionic liquids with higher melting points. By  
15 reducing the extracted liquid phase temperature to a  
sufficiently low level, the ionic liquid is solidified in  
a non-crystalline form.

According to one embodiment of the invention, a separate  
20 stream of the liquid phase, from which the solids have  
been separated, is directly recycled to an upstream stage  
of the process for contacting with further lignin-  
containing material without any removal of lignin.

25 The diluted stream of ionic liquid, from which the  
precipitated lignin has been removed, may be dewatered to  
remove excess water (added during dilution) therefrom.  
Thereafter, the dewatered ionic liquid may be subjected to  
distillation to remove other chemicals extracted from the  
30 lignin-containing materials therefrom. These other  
chemicals may include acetic acid and/or furfural.  
Thereafter, the ionic liquid is recycled for contacting  
with further lignin-containing material.



*Other features of the ionic liquids*

The new ionic liquids identified in the present  
5 application also display high electrochemical stability  
compared to conventional electrolytes. Typically large  
electrochemical windows are observed using cyclic  
voltammetry. Ionic liquids of this type are therefore also  
suitable for use as electrolytes, or ionic additives, for  
10 electrochemical applications such as electrowinning  
technologies. Any metal salt, including; copper, titanium,  
and aluminium, that can be dissolved in the ionic liquid  
and electrochemically reduced is potentially recoverable  
in the metallic form.

15

Examples

The present invention will now be described in further  
20 detail with reference to the following non-limiting  
examples.

*Synthesis of novel materials*

25 Ionic liquids were generally prepared by heating  
constituent salts in toluene to allow a metathesis  
reaction to proceed to yield the target ionic liquid.

Example 1

30 1-ethyl-3-methylimidazolium xylenesulfonate (EmImXS) was  
prepared by metathesis of sodium xylenesulfonate and 1-  
ethyl-3-methylimidazolium bromide.

EmImXS is a useful liquid salt for the extraction of  
35 lignin from pulp at temperatures around 150°C in a solvent  
mixture which contains water and some residual sodium  
xylenesulfonate.

The procedure for the production of EmImXS was the same as that used for the production of tetrabutylammonium xylenesulphonate (TBABXS) from tetrabutylammonium bromide and sodium xylenesulphonate, and tetrabutylammonium benzoate (TBABBz) from tetrabutylammonium bromide and sodium benzoate.

This procedure involved the following steps. Approximately equimolar amounts of 1-ethyl-3-methylimidazolium bromide or tetrabutylammonium bromide and sodium xylenesulphonate were added to a 2-litre round bottom flask. Toluene (600 ml, 5-6 times the mass of salts) and boiling chips were added to the flask. The flask was fitted with a condenser and the slurry was heated at reflux overnight. Upon cooling, the slurry was filtered to remove the sodium bromide metathesis product. The filtrate was evaporated to dryness on a rotary evaporator to give a thick viscous liquid. Acetone was added to the flask and the ionic liquid was dispersed with vigorous mixing. The solution was filtered and the filtrate was evaporated to dryness once more. The resultant ionic liquid was left to rotate on the rotary evaporator at a very low speed and at high temperature (~90°C) to remove as much residual toluene as possible. The residual oil was then used as neat ionic liquid.

#### Example 2

Trihexyltetradecylphosphonium xylenesulfonate (P66614XS) was prepared using two different methods.

In a first method, an ion-exchange column was loaded with xylenesulfonate anions and a solution of trihexyltetradecylphosphonium chloride was passed through several times until complete exchange was indicated by the lack of chloride ions in the eluent. <sup>1</sup>Hnmr (CDCl<sub>3</sub>) δ 0.85-0.95 (m, 12H, CH<sub>3</sub>), 1.20-1.35 (m, 48H, CH<sub>2</sub>), 1.40-1.60 (m,

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14H, P-CH<sub>2</sub> & Ar-CH<sub>3</sub>), 6.90-7.30 & 7.60-7.90 (m, 3H, CH).  
Electrospray Mass Spec: ES+ 483 [P66614+] m/z. ES- 185  
[XS-] m/z.

5 According to the second method,  
trihexyltetradecylphosphonium chloride (P66614 chloride;  
1.1 mole) was refluxed with 1 mole of sodium  
xylenesulfonate (NaXS) in toluene overnight. The product  
was filtered and toluene removed by rotary evaporation  
10 under vacuum to recover the ionic liquid. The ionic liquid  
was characterized by NMR/ES MS.

This phosphonium cation based hydrophobic ionic liquid was  
synthesised because it precludes water which may  
15 facilitate removal of inorganics such as silica into the  
water phase during extraction of lignocellulose materials  
and also would make it suitable for use in some noble  
metal electrochemical extraction applications. In  
addition, the asymmetric nature of cation produces a  
20 liquid substance at room temperature.

P66614XS was tested and found to display excellent thermal  
stability at 150 °C. Thermogravimetric analysis indicates  
the loss of less than 0.2% volatile material during 4  
25 hours at this temperature. Thermal decomposition  
temperature was calculated using the step-tangent method  
and found to be 310°C.

### Example 3

30 Tetrabutylammonium dodecylbenzenesulfonate N4444DDBS is  
prepared by neutralising an aqueous solution of  
dodecylbenzenesulfonic acid with tetrabutylammonium  
hydroxide and removing water by evaporation.

### Example 4

35 N-butyl-N-methylpyrrolidinium 4-hydroxybenzenesulfonate is  
prepared directly in one-pot by alkylating N-

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butylpyrrolidine with the methyl ester of 4-hydroxybenzenesulfonic acid.

#### Example 5

5 Tetrabutyl ammonium xylenesulfonate (N4444 XS) was prepared by a reflux reaction between tetrabutyl ammonium bromide (N4444 Br) and sodium xylenesulfonate (solid) in toluene for 10-12 hours. The product was filtered and the toluene evaporated from the reaction mixture, followed by  
10 washing with acetone to yield the pure ionic liquid. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): ppm 0.9 (t, *J* = 7.5 Hz, 12H, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N), 1.12-1.26 (m, 8H, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N), 1.4-1.54 (m, 8H, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N), 2.18 (s, 3H, Xy-CH<sub>3</sub>), 3.00 (s, 3H, Xy-CH<sub>3</sub>), 3.01 (t, 8H, *J* = 8.4 Hz (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N),  
15 6.99-7.3 (m, 2H, Xy-H), 7.51-7.59 (m, 1H, Xy-H).

N4444 XS is a hydrophilic ionic liquid. Being hydrophilic, this ionic liquid can penetrate the wood chips and extract lignin effectively.

20

#### Example 6

Phenyltrimethylammonium xylenesulfonate (Ph(Me)<sub>3</sub>N XS) ionic liquid was prepared in a reflux reaction between phenyltrimethylammonium chloride (Ph(Me)<sub>3</sub>N Cl) and sodium  
25 xylenesulfonate (NaXS; solid) in toluene for 10-12 hours. The product was filtered and evaporated toluene from the reaction mixture to yield a crude solid product. The crude ionic liquid was washed with DCM to remove impurities.

30 *Testing and Use of novel materials*

#### Example 7

An extraction process was carried out as follows:

A reaction vessel is charged with a solution of ionic  
35 liquid based solvent. Biomass such as wood chips or herbaceous material are added to the vessel. The mixture is heated and stirred for several hours. Solid cellulosic

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material is filtered and prepared for pulping to paper. Dilution of the filtrate after repeated digestion cycles with water precipitates lignin, which is collected. Distillation of the filtrate affords various volatile  
5 chemicals. The ionic liquid based solvent is recycled to the beginning of the process.

In the above process, the following specific conditions and materials were used.

10

Bagasse was used as a prototype biomass. Bagasse has the following average composition on a dry weight basis: Cellulose 41%; Hemicellulose 23.2%; Lignin 21.2%; Ash 10.9%; Extractives 4.5%

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2.58 grams of sifted (2-3 mm mesh) bagasse was combined with 22.62grams of tetrabutylammonium xylene sulphonate, 2.5 grams of water and sufficient acetic acid to bring the pH to 4.0 in a 100ml round bottom flask. This mixture was  
20 subjected to an impregnation step, 90 minutes refluxing at 130°C. The temperature of the mixture was then increased to 160°C by removing the reflux condenser to allow excess water to evaporate. The reflux condenser was replaced and the mixture subjected to digestion at 160°C for 2 hours.  
25 Upon reaction termination the solid bagasse pulp was removed by filtration, the filter cake being subjected to washing with water (x2 100ml) and acetone (x1 50ml). All filtrates were then combined and 600ml of warm water added to precipitate the extracted lignin and cellulose  
30 materials. This reaction produced 1.24g of digested bagasse and 1.2g of lignin/cellulose extract (95% mass retention).

#### Example 8 - Extraction trials

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General procedure.

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The following procedure was used in the extraction trials, with the exception of P66614XS where the mass was reduced.

Ionic liquid was warmed to assist in its transfer to the  
5 reaction flask. The IL (~90 g) was added to a 250-ml two-necked round bottom flask and the IL mass was recorded. Water (~10 g) was added and the flask was swirled to mix the contents evenly. Acid or base was added to the flask as required and the amount of acid or base was recorded.  
10 Bagasse (~10 g) was added and the flask was warmed to help ensure that the bagasse was thoroughly wetted by the IL solution. The flask was fitted with a reflux condenser (and a stopper in the second neck) and heated in an oil bath at reflux for 1 hour. The condenser was then  
15 replaced with a stillhead, to which the condenser was reattached. The temperature of the oil bath was then increased to drive the distillation of water and residual toluene from the reaction flask. The distillate was recovered in a tared collection flask. The temperature  
20 within the reaction flask rose to 150°C and it was maintained in the range of 150°-160°C for 2 hours. The distillation apparatus was then dismantled and the masses of the distillate and residue were recorded. The residue was diluted with acetone (200 ml) and filtered (Whatman  
25 no. 1) while still hot. The residual pulp was washed with further acetone until the filtrate appeared near colourless. The pulp was washed with water and more acetone and was then oven-dried. The combined filtrates were then evaporated to remove water and acetone, and the  
30 black oily residue that remained was weighed. It was assumed that this residue contained the recovered IL and the extracted lignin.

## Results

The results for the cooking experiments are shown in  
5 Tables 1 and 2. Table 1 shows a general mass balance for  
each experiment, while Table 2 more specifically shows the  
performance in extracting lignin from bagasse and the  
recovery of the ionic liquid.

## 10 Notes

- It is apparent from mass balance results obtained  
following digestion of the bagasse that the cellulose  
and hemicellulose in the pulp generally suffered little  
15 degradation, which indicates that ionic liquid pulping  
is highly selective for lignin extraction.
- Lignin was not separated from the ionic liquid after  
separation from the pulp. The degree of lignin removal  
was calculated based on the Kappa number of the  
20 resultant pulp.
- The high recovery of EMIMXS was related to the low  
toluene content in the ionic liquid before the cooking  
trial. Toluene was not collected in the distillate for  
the EMIMXS trials. In contrast, several grams of  
25 toluene was collected in the distillate for the trials  
using TBAXS and TBABz. This probably explains the yield  
of recovered IL for the TBAXS trials.
- The results with TBABz were not as good as for the other  
ionic liquids. The smaller quantities of TBABz used in  
30 these trials also contributed to experimental inaccuracy  
for this ionic liquid. Furthermore, on completion of  
the trials with TBABz, a strong ester-like odour was  
evident, suggesting that some chemical transformation  
had occurred.
- 35 • Acidic trials appeared to be more efficient as judged by  
eye and from the Kappa number results.

**Table 1.** Overall mass balance for ionic liquid extractions of bagasse

Ionic liquid	Bagasse in (wet) <sup>a</sup>	Dry bagasse	pH	IL	Added water	Acid/base	pH	Total in	Residue	Pulp	IL + lignin	Distillate	Total out	Overall loss (%)
EMIMXS	10.03	6.50	6	90.04	10.17	0	6	110.24	98.69	5.61	92.62	7.28	105.51	4.29
EMIMXS	10.38	6.73	4	90.11	10.35	0.37	4	111.21	99.2	5.53	91.52	8.06	105.11	5.49
TBAXS	10.06	6.52	4.5	87.85	10	0.43	4.5	108.34	85.52	4.87	80.1	15.89	100.86	6.90
TBAXS	10.05	6.51	9	90.45	10	0	9	110.5	88.05	5.25	76.86	15.35	97.46	11.80
TBABz	3.94	2.55	7	35.03	3.94	0	7	42.91	31.22	1.97	17.29	5.72	24.98	41.79
TBABz	4.03	2.61	4.5	34.96	3.94	0.2	4.5	43.13	31.24	1.8	19.87	7.64	29.31	32.04
P66614XS	0.724	0.47	7	6.29	0.715	0	7	7.729	6.705	0.22	6.46	1	7.68	0.63%

EMIMXS, ethylmethylimidazolium xylenesulphonate; TBAXS, tetrabutylammonium xylenesulphonate; TBABz, tetrabutylammonium benzoate; P66614XS, trihexyltetradecylphosphonium xylene sulphonate

<sup>a</sup> Bagasse moisture: 35.2%

**Table 2.** Efficiency in removal of lignin from bagasse and recovery of ionic liquids

Ionic liquid	Bagasse in (wet)	Dry bagasse	pH	IL	IL + lignin	Pulp	Pulp kappa	% Lignin in pulp <sup>a</sup>	Lignin in pulp	Total available lignin <sup>b</sup>	% Lignin removed	Recovery d IL (%) <sup>c</sup>
EMIMXS	10.03	6.50	6	90.04	92.62	5.61	48.05	7.21	0.40	1.38	0.97	102%
EMIMXS	10.38	6.73	4	90.11	91.52	5.53	61.1	9.17	0.51	1.43	0.92	101%
TBAXS	10.06	6.52	4.5	87.85	80.1	4.87	55.6	8.34	0.41	1.38	0.98	90%
TBAXS	10.05	6.51	9	90.45	76.86	5.25	60.9	9.14	0.48	1.38	0.90	84%
TBABz	3.94	2.55	7	35.03	17.29	1.97	57.9	8.69	0.17	0.54	0.37	48%
TBABz	4.03	2.61	4.5	34.96	19.87	1.8	53	7.95	0.14	0.55	0.41	56%
P66614XS	0.724	0.47	7	6.29	6.46	0.22	41.4	6.21	0.01	0.10	0.09	101%

<sup>a</sup> Based on formula (% lignin =  $0.15 \times \text{Kappa no.}$ )

<sup>b</sup> Assumed lignin content in bagasse ~21.2% on dry weight

<sup>c</sup> Based on lignin recovery as calculated by Kappa number determination



Example 9 - Continuous Process

Figure 1 illustrates a continuous process for conducting the process of one embodiment of the invention.

5

Biomass is prepared 1 and fed into a digester 2 together with ionic liquid from two different sources, as will be described in further detail below.

10 The digester 2 is heated by a boiler 3. The lignin is extracted from the biomass into the ionic liquid in the boiler. Thereafter, the material from the digester is washed/refined 4, and subjected to solid/liquid separation 5. The solid cellulosic fibre is recovered 6 and used for  
15 paper production or similar. The ionic liquid is separated into two streams - a first stream (2/3 of the ionic liquid) being recycled 7 to the digester 2, and the second (1/3 of the ionic liquid) being sent to lignin precipitation process step 8. The precipitated lignin is  
20 separated from the ionic liquid by liquid/solid separation 9, and the lignin recovered 10 for various end uses. One possible use represented by the dashed line is as fuel for the boiler 3. The ionic liquid is then dewatered 11, prior to distillation/concentration 12 to recover organic  
25 byproducts 13 such as furfural and acetic acid. Water removed during dewatering 11 is recycled to the washing/refining stage 4. The ionic liquid from the distillation/concentration stage is regenerated 14 for recycling to the digester 2.

30

It will be understood to persons skilled in the art that many modifications may be made to the embodiments and Examples described above without departing from the spirit and scope of the invention.